



Short communication

Evaluation of real performance of LiFePO_4 by using single particle technique

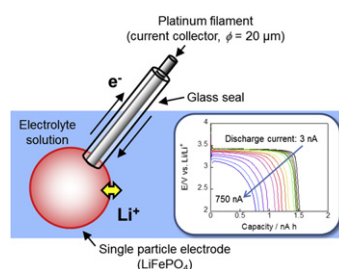
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HIGHLIGHTS

- Single particle measurement was carried out for LiFePO_4 secondary particle.
- 50% of the full capacity was maintained even at 4 s discharge (900 C rate).
- Li^+ diffusion coefficient in the particle was estimated to be $2.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

GRAPHICAL ABSTRACT



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ABSTRACT

Single particle technique was employed to investigate the intrinsic electrochemical properties of LiFePO_4 . A micro-size LiFePO_4 single particle composed of a plurality of primary particles was contacted with a micro Pt electrode in an electrolyte solution using a micromanipulator under optical microscope observation, and then galvanostatic charge/discharge tests were performed. The specific capacity of the particle with a diameter of $24 \mu\text{m}$ was estimated to be 1.5 nA h in the potential range of $2.0\text{--}4.2 \text{ V vs. Li/Li}^+$. The particle had a good reversibility for charge/discharge processes, and also showed excellent rate performance, for example, that more than 50% of the full capacity was maintained even when the discharge current was as high as 750 nA corresponding to 4 s discharge (900 C rate). From the dependency of over-potential in the single particle electrode on discharge current density, it was expected that the discharge reaction was controlled at the discharge current densities higher than 2.56 mA cm^{-2} by Li^+ diffusion step in the particle accompanied with the phase conversion from FePO_4 to LiFePO_4 . According to this assumption, Li^+ diffusion coefficient in the particle was estimated as $2.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

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1. Introduction

Lithium-ion batteries are widely used as power sources for portable electronic devices such as laptop computers and cellular phones due to their high energy density. The requirements for batteries are becoming more intensive. Especially, new applications including electric vehicles (EVs) and hybrid electric vehicles (HEVs) have much higher energy and power requirements [1,2]. In order to meet the upcoming demands, many research groups are focusing

on the development of new active materials with higher performances. For example, lithium transition-metal phosphates with olivine-type structures have recently attracted much attention as promising cathode materials due to their lower toxicity, lower cost, environmental compatibility, and high safety [3–8]. $\text{Li}_2\text{MnO}_3\text{--LiMO}_2$ ($M = \text{Co, Ni, Mn}$ etc.) solid solutions have also been attracted attention in recent years as next generation cathode materials with high specific capacity [9,10]. So far, active materials have been evaluated as porous composite electrodes prepared by mixing with organic polymeric binder and conducting materials [11,12]. However, the additives, i.e. polymer binder and conducting materials, in the porous composite electrode have been reported to affect the charge/discharge properties. The electrode structures

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such as porosity and thickness also influence on the electrode performance, because there are distributions of electric potential, current density, and Li^+ concentration within the electrode during charging and discharging [13]. These distributions become particularly significant in the cases of high rate charging and discharging, and then the electrochemical reaction does not take place uniformly within the porous composite electrode. Therefore, the electrochemical responses of conventional porous composite electrode are “apparent”, not “intrinsic” for the active material. This situation sometimes makes it difficult to estimate and to draw the real performance of new active materials thoroughly.

In addition to preparation of new active materials, theoretical designs of porous composite electrodes are actively being conducted for improving battery performance [14–20]. This kind of researches have particularly been done for scaling up of battery size, since they provides much information about the dynamics of batteries, which is helpful to develop not only an ideal electrode structure for fully utilizing the potential of active material but also a better battery management system to ensure the safety of batteries. The theoretical calculations are performed based on simplified electrode models, for which precise parameters about the properties of cell components such as diffusion coefficients of Li^+ in active material and electrolyte solution are needed as well as structural parameters of composite electrode. However, as mentioned above, the parameters concerning electrochemical properties of active materials have been collected using conventional porous composite electrodes, resulting in the deviation of calculations from the experimental values.

In our previous study, we employed “single particle technique” to evaluate electrochemical properties of LiCoO_2 and graphite [21,22]. This technique enables to evaluate the electrochemical responses of a single particle of active material without binder and conducting materials. Therefore, the effects of additives and electrode structure on the performance of active material can be ignored. Furthermore, in the case of single particle, the current in electrochemical polarization measurements is small enough that the IR drop can be neglected even if the material is highly resistive. Then, the distributions of electric potential and current density are almost uniform at the particle surface, allowing accurate determination of the intrinsic performance of active material. Actually in our previous study, it was clarified that LiCoO_2 particle (diameter: 8 μm) had the performance to operate at the full discharge capacity up to a high rate of 30 C [21]. In this study, we focus on LiFePO_4 , which is considered as a promising cathode material for large-scale batteries due to its safety characteristics and cycleability, and precisely investigate its electrochemical performance using the single particle technique.

2. Experimental

All measurements were carried out in a glove box filled with dry argon at room temperature. Pt electrode with 20 μm diameter was attached to a target particle in an electrolyte using a micromanipulator under optical microscope observation, and then the electrochemical measurements were performed with a two-electrode system using 1 cm^2 Li foil as a counter electrode. The details are in our previous reports [21–23]. The Pt micro-electrode was sealed with glass to minimize background current before use as shown in Fig. 1. The procedure for fabricating the glass-sealed electrode was reported by Shiku et al. [24]. LiFePO_4 particle used in this study was non-doped and carbon-coated one supplied from Sumitomo Osaka Cement Co., Ltd. A mixed solvent of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 in volume) containing 1 mol dm^{-3} LiClO_4 was used as the electrolyte solution. Charge/discharge tests were carried out using an electrochemical analyzer (ALS model

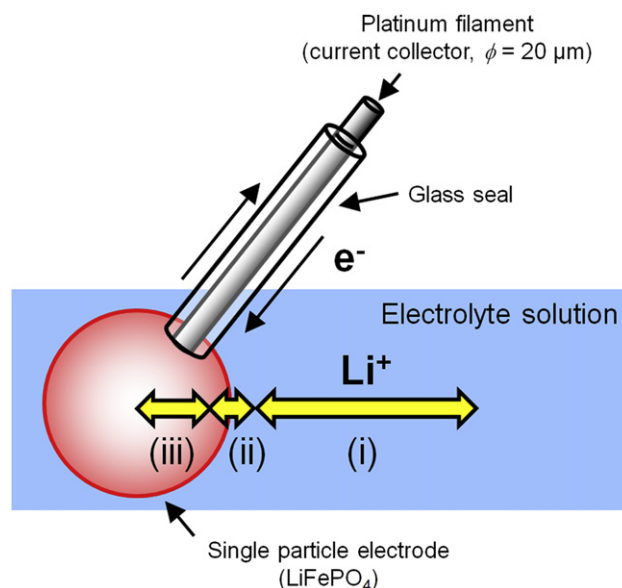


Fig. 1. Schematic illustration of single particle measurement. During the discharge reaction, the following steps occur; (i) Li^+ diffusion to the particle surface from a bulk electrolyte solution, (ii) Li^+ transfer at the particle/electrolyte solution interface (interfacial charge transfer), (iii) Li^+ diffusion from the surface to center of the particle.

660A, BAS) in the potential range of 2.0–4.2 V vs. Li/Li^+ . All the tests were conducted at 30 $^{\circ}\text{C}$.

3. Results and discussion

Fig. 2 shows the typical image of LiFePO_4 particle, observed with a scanning electron microscope (SEM). It was found that LiFePO_4 used in this study was a spherical secondary particle composed of a plurality of primary particles. The primary particles were 100–200 nm in diameter and well-bonded together to act as a single particle. Their strong association was actually confirmed by contact with Pt micro-electrode in electrochemical measurements.

Fig. 3 shows charge and discharge curves of a LiFePO_4 particle during the initial three cycles, measured at 3 nA for both charging and discharging processes. The size of particle was 24 μm in

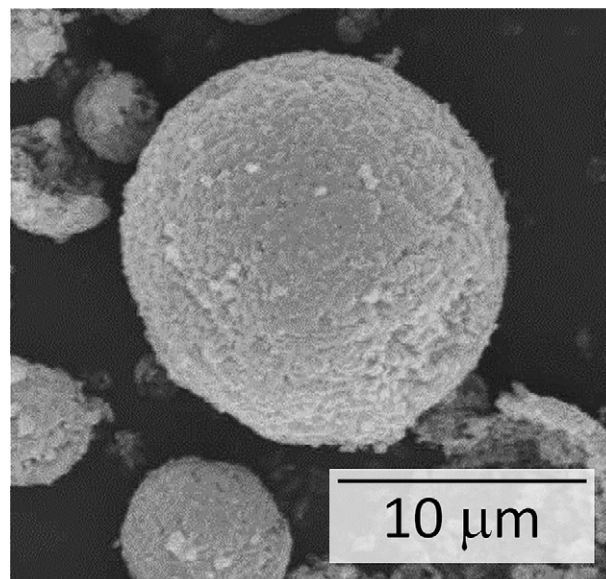


Fig. 2. SEM image of LiFePO_4 particle evaluated in this study.

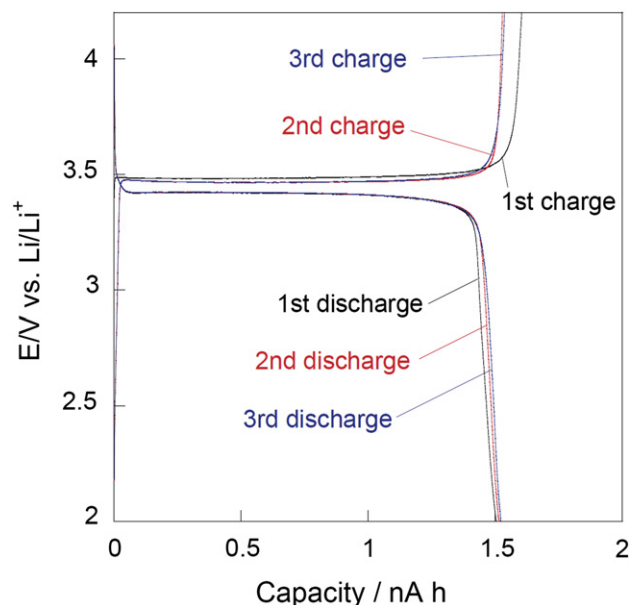


Fig. 3. Charge/discharge curves for the LiFePO_4 single particle electrode measured at 3 nA and 30°C .

diameter. Although the first cycle showed a little irreversible capacity, high coulomb efficiency was obtained after the second cycle. From the second cycle, the single particle electrode exhibited excellent reversibility, and then the specific discharge capacity for the single particle was estimated to be 1.5 nA h. According to this specific discharge capacity, the apparent volume capacity of LiFePO_4 particle can be calculated as 207 mA h cm^{-3} on the assumption that the particle is completely spherical. The calculated value is about one-third of the theoretical volumetric capacity (612 mA h cm^{-3}). This deviation is expected to be due to the error in particle size estimation since the actual LiFePO_4 particle was not perfectly spherical. Also, it can be considered that the particle included some vacancies as shown in the right below of Fig. 2, which may be another main reason for the capacity deviation.

Fig. 4 shows discharge curves of LiFePO_4 particle measured at various currents. The particle was charged galvanostatically at a constant current of 3 nA up to 4.2 V vs. Li/Li^+ , prior to each discharge measurement. The specific capacity of LiFePO_4 particle was 1.5 nA h as estimated above. Therefore, the charge and discharge at the current of 3 nA corresponds to 2 C rate. Actually, 1827 s were spent in the full discharge at 3 nA. As shown in Fig. 4, the LiFePO_4 particle exhibited excellent rate capability and maintained more than 90% of the full capacity at 10 nA discharge (515 s). Also even at 750 nA discharge (only 4 s), more than 50% of the full capacity was maintained. Furthermore, it was confirmed in the charge processes that the LiFePO_4 particle had excellent reversibility for charging and discharging, namely the capacity was completely recovered to the full capacity of 1.5 nA h even after discharges at high rates (Fig. 5). These electrochemical responses are greatly better than those reported for the composite electrode [25,26]. During the discharge reaction, the following steps occur; (i) Li^+ diffusion to the particle surface from a bulk electrolyte solution, (ii) Li^+ transfer at the particle/electrolyte solution interface (interfacial charge transfer), (iii) Li^+ diffusion from the surface to center of the particle. Here, the step (iii) should be accompanied with the phase transition from FePO_4 to LiFePO_4 according to the increment of x from 0 to 1 in Li_xFePO_4 . The Li^+ diffusion in a solid phase (particle) is generally slower than that in a liquid phase (electrolyte solution). Therefore, the rate determining step is (ii) or (iii). As

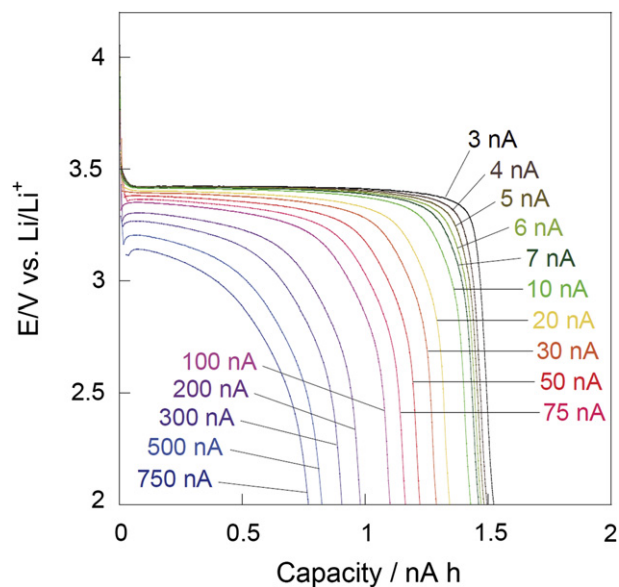


Fig. 4. Rate capability of the LiFePO_4 single particle electrode at 30°C . The particle was charged galvanostatically at a constant current of 3 nA up to 4.2 V vs. Li/Li^+ , prior to each discharge measurement.

discussed in our previous paper, if there is a large gradient of Li^+ concentration in the particle during the discharge reaction, the electrode potential drops to cut-off potential rapidly when x in Li_xFePO_4 reaches 1 at the particle surface while x at the center of particle does not reach 1. In such case, the full discharge capacity is not accomplished, and the reaction rate is controlled by Li^+ diffusion in the solid phase of (iii). As shown in Fig. 4, the LiFePO_4 particle had more than 95% of the full capacity at the discharge current of 10 nA or less. Therefore, it is inferred that there is little gradient of Li^+ concentration in the particle during the low current discharges and the reaction rate is controlled by the interfacial charge transfer step of (ii). On the contrary, a gradual decrease of the discharge capacity was observed at high discharge currents.

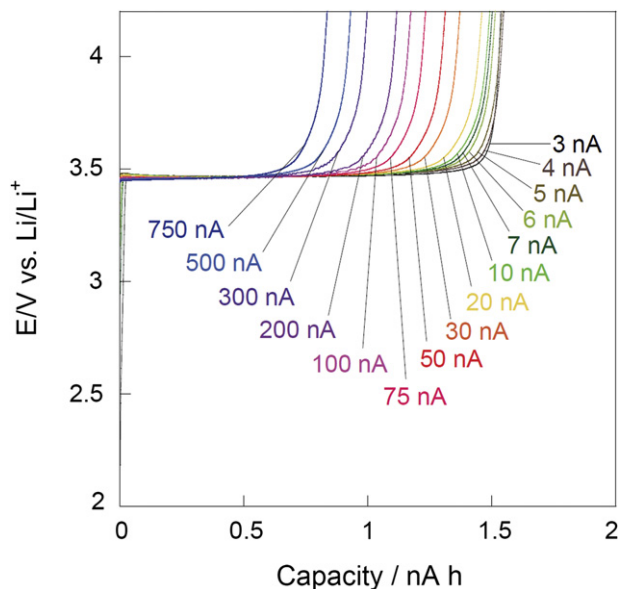


Fig. 5. Charge curves for the LiFePO_4 single particle electrode after the discharges at different currents (3–750 nA) shown in Fig. 4, respectively.

This behavior is considered as the situation that the reaction rate is controlled by (iii) Li^+ diffusion from the surface to center of the particle.

To reveal this aspect more clearly, the potential (E) of LiFePO_4 single particle electrode at the half discharged state was plotted against the logarithm of each discharge current ($\log i$) in the rate performance test shown in Fig. 4. In this study, the transfer coefficient α between charging and discharging reactions was assumed as 0.5. A clear correlation interpreted by quasi Tafel equation was confirmed between i and E as shown in Fig. 6, in which each discharge current was normalized to an apparent surface area of the measured particle. An exchange current density (i_0) for the LiFePO_4 particle was estimated to be 0.27 mA cm^{-2} by fitting a straight line of Tafel equation with $\alpha = 0.5$ and its extrapolation to the equilibrium potential of 3.44 V vs. Li/Li^+ . In addition, the slope became gentle as E shifted from the equilibrium potential to the negative side. This results suggests that another linear relation exists between $\log i$ and E . As discussed above, the electrochemical reaction rate of LiFePO_4 single particle should be governed by either (ii) Li^+ transfer at the particle/electrolyte solution interface or (iii) Li^+ diffusion from the surface to center of the particle, and the different dependencies of $\log i$ on E observed in Fig. 6 can be considered to be the shift of rate determining step from (ii) to (iii). Therefore, if it is assumed that the highest i (2.56 mA cm^{-2}) on the fitting line is the threshold to decide the rate determining step, Li^+ diffusion coefficient in the particle can be estimated from a three-dimensional diffusion model. In the case of three-dimensional diffusion, the diffusion length L can be expressed as $L = (6Dt)^{1/2}$, where D is the diffusion coefficient. The particle radius is considered as the diffusion length L of Li^+ in the particle, and the diffusion time t is the time required for full discharging of the particle. When the particle (diameter: $24 \mu\text{m}$) was discharged at 2.56 mA cm^{-2} , the duration for Li^+ diffusion from the surface to center of the particle was 88 s, providing $2.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ as the D value. This value is several orders of magnitude larger than those reported previously, which is expected to be due to the difference in the system of measurement since the previous ones have been obtained for conventional composite electrodes [27–30]. Therefore, the D value estimated in this study is basically different from the previous ones including structural and compositional effects of composite electrode. Actually, it was reported by Liu et al. that the D value of $9.98 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ in LiFePO_4 greatly increased to $1.01 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ and then $4.89 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in the $\text{LiFePO}_4/\text{carbon}$ composite as increasing the carbon content from 5 wt% to

20 wt% [28]. This result clearly demonstrates the difficulty in investigation of real properties of active materials by using conventional composite electrodes. On the other hand, the D value estimated in this study is in good agreement with the theoretical values ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for LiFePO_4 and FePO_4 , respectively) calculated by Morgan et al. using first-principles methods [31]. The particle measured in this study was a secondary particle composed of a plurality of primary particles, so that the obtained value actually represents the D value in secondary particle, not in a primary particle. However, this value is useful for a brief evaluation of the potential of LiFePO_4 , and is especially available for designing the composite electrode since this kind of secondary particles are practically used in the electrode preparation instead of small primary particles. In our previous study, the apparent D value for Li^+ diffusion in LiCoO_2 secondary particle was estimated to be larger than $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ [21]. Then, it can be inferred that the Li^+ diffusion in LiFePO_4 accompanied with the phase-transition between FePO_4 and LiFePO_4 is same or a little faster than that in LiCoO_2 . This result suggests that the rate performance of LiFePO_4 is intrinsically excellent. In other words, a poor rate performance of LiFePO_4 , which is usually observed in the composite electrode, is considered to be caused by secondary factors such as the lack of electron conductivity and Li^+ diffusion in the composite electrode.

4. Conclusions

As demonstrated here, the single particle measurement can provide many kinds of new insights for designing composite electrodes of lithium lithium-ion batteries, which are essential to develop future large-scale batteries as well as theoretical approaches based on computational models. The electrochemical properties of LiFePO_4 were investigated using the single particle technique, and it was found that LiFePO_4 had excellent rate capability as well as LiCoO_2 . For example, 90% of the full capacity was maintained at 10 nA discharge corresponding to 7 C rate (515 s), and more than half of the full capacity was kept even at 750 nA discharge (only 4 s) in LiFePO_4 single particle with a diameter of $24 \mu\text{m}$. On the assumption based on quasi Tafel equation that 2.56 mA cm^{-2} was the threshold current density for switching the rate determining step of discharge reaction from an interfacial charge transfer process to Li^+ diffusion in the particle, the Li^+ diffusion coefficient was estimated to be $2.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. This value is several orders of magnitude larger than those reported previously and is comparable to that in LiCoO_2 , suggesting that LiFePO_4 intrinsically has excellent rate capability but its potential is hardly utilized in the porous composite electrodes. The single particle measurement is applicable to not only a primary particle but also a secondary particle, so that the real electrochemical properties of many kinds of secondary particles used in practical electrodes can be investigated. We hope that this method can pave the way for future design of lithium-ion batteries.

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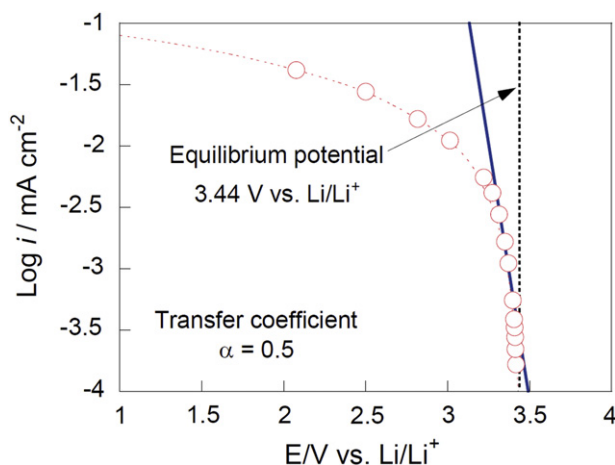


Fig. 6. The potential dependency of LiFePO_4 single particle electrode on discharge current density at 30°C . The fitting line shows the Tafel equation with $\alpha = 0.5$.

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